

PRELIMINARY STUDY OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR A VENUS MISSION. Z. A. Arp¹, D. A. Cremers², R.C. Wiens³, ¹Nuclear Materials and Technology, Los Alamos National Laboratory (MS J565, Los Alamos, NM 87545 USA; zaa@lanl.gov), ²Advanced Chemical Diagnostics and Instrumentation, Los Alamos National Laboratory (MS J565, Los Alamos, NM 87545 USA; cremers_david@lanl.gov), ³Space and Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545 USA; rwiens@lanl.gov).

Introduction: Laser-Induced Breakdown Spectroscopy (LIBS) has been proposed as a candidate analysis system for missions to Mars, asteroids, and recently Venus. This technique has several distinct advantages over other techniques which have been used on past missions (X-Ray fluorescence on Viking 1 and 2, 1976; APXS on Pathfinder, 1997; MER, 2004). Two of the more important advantages LIBS has over other techniques for a mission to Venus is rapid elemental analysis of both high and low Z value elements and stand-off analysis at distances of many meters.

Rapid elemental analysis and stand-off analysis are very important to missions to Venus due to the harsh environment at the planet surface. From the Venera missions it is known that on the Venusian surface the pressures are approximately 9.1 MPa (90 atm) and the temperature is near 735 K [1]. For these reasons, the Soviet Venera surface probes had operational lifetimes of less than 2 hours. Currently Venus is the target of one of four missions specifically mentioned for consideration for NASA's New Frontier Program with a launch date of 2010 or earlier. In light of this, it is beneficial to evaluate different analysis methods such as LIBS, which offer to greatly increase the scientific return from such a mission.

Currently we have begun to evaluate LIBS detection in an environment with pressures and compositions which are similar to those found on Venus. Although the temperature of Venus (~735 K) has not been taken into account in these experiments, due to the high temperature of the plasma (~8000 K) significant perturbations of excitation characteristics sufficient to affect LIBS analytical capability would not be expected. Previous work, however, has shown that the pressure of the surrounding atmosphere can have a strong effect on the detection of elements in a solid [2,3]. These studies have mainly concentrated on pressures at or below earth ambient pressure, but one study has shown successful results at elevated pressures (3.0 MPa) [4]. Here we show results from a LIBS study at 9.1 MPa (90 atm) which demonstrates the feasibility of using this technique for elemental analysis at high pressure.

Experimental: Fig. 1 shows the experimental setup used for testing LIBS at high pressures. The high pressure cell consisted of a steel chamber (40 W x 40.3

L x 19 H cm outside) with a cylindrical cavity (9.8 cm diam) milled through the center of the steel block. Windows were made of sapphire (6.35 cm diam x 3.175 cm thick) with highly polished front and back

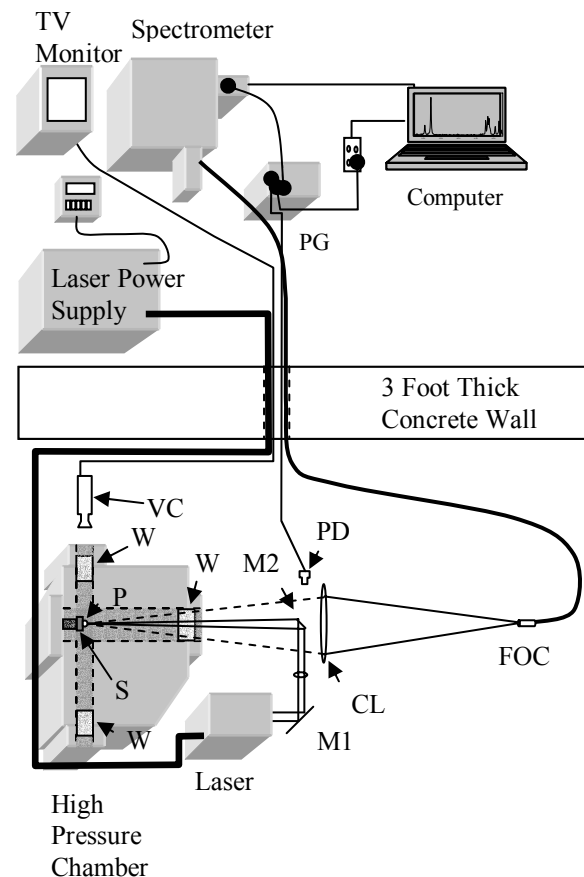


Fig. 1 Experimental Setup used to evaluate LIBS at high pressure. PG= Pulse Generator; VC=Video Camera; P=Plasma; S=Sample; M1 and M2=Mirror 1 and 2; CL= 1m Focal Length Collection Lens; W=Sapphire Window; PD= Photodiode; FOC= Fiber Optic Cable

surfaces. A basalt rock sample was used as the target for these experiments. Nd:YAG lasers were used for excitation and either a Chromex 250 IS spectrograph or a Catalina Sciences SE200 echellette spectrograph were used for light dispersion and detection. CO₂ and N₂ were used for pressurization of the high pressure

cell. Although the atmosphere at the surface of Venus is mainly composed of CO₂, in these experiments N₂ was used to pressurize the system above 5.7 MPa since CO₂ at or below room temperature liquefies above this value. N₂ was chosen as the surrogate for CO₂ in these experiments because it is relatively inert and has few atomic emission lines which minimizes interferences, much like CO₂.

Results: In this work several experiments were performed to determine the characteristics of LIBS under different operational parameters. Characteristics of LIBS signals were investigated while varying parameters such as laser power, pressure, delay timing, and atmospheric gas (CO₂ and N₂). A major concern in detecting the LIBS signal is the potential for absorption of light by the high pressure gases used here. Using a Hg spectral calibration lamp and a tungsten radiance calibration lamp, we were able to determine if these gases, at high pressure, exhibited absorption in the region of interest for monitoring element LIBS emissions (200-800 nm). Neither of these gases showed absorption in the 200-800 nm region.

The reduction in the size of the plasma produced under low and high pressurization conditions is shown in Fig. 2. As can be seen, the size of the plasma decreases somewhat as the pressure is increased. The plasma, although smaller, was still analytically useful.

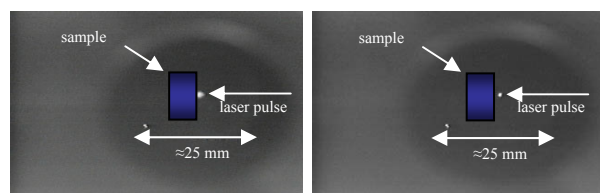


Fig. 2 Photo of laser plasmas formed on basalt at (a) .078 MPa (0.77 atm) and at (b) 9.1 MPa (90 atm) of N₂.

Shown in Fig. 3 are spectra taken at pressures ranging from 9.1 MPa (90 atm.) down to 0.077 MPa (0.77 atm.). As seen in this figure, the LIBS spectra of Al and Ca lines show pressure broadening and self-absorption at the elevated pressures when compared to spectra taken at atmospheric pressure. Other lines (Fe, Sr, Mn, etc.) show little change with pressure. The observed broadening and the self-absorption are both expected results from the elevation in pressure for emission lines, such as those from Al and Ca, having low lying upper energy levels. Data taken while varying either the delay time or the laser power show similar elemental lines as those shown in Fig. 3. The major differences between spectra taken varying these parameters is in the intensities of the lines observed.

Fig. 4 shows a comparison between spectra taken in CO₂ and N₂ gases. As can be seen in this figure, the broadening and self absorption seen in the N₂ environment are not as prevalent in the CO₂ environment. This indicates that LIBS may exhibit better characteristics for LIBS detection at the pressures found on Venus in a CO₂ environment than are shown for the N₂ environment in Fig. 3.

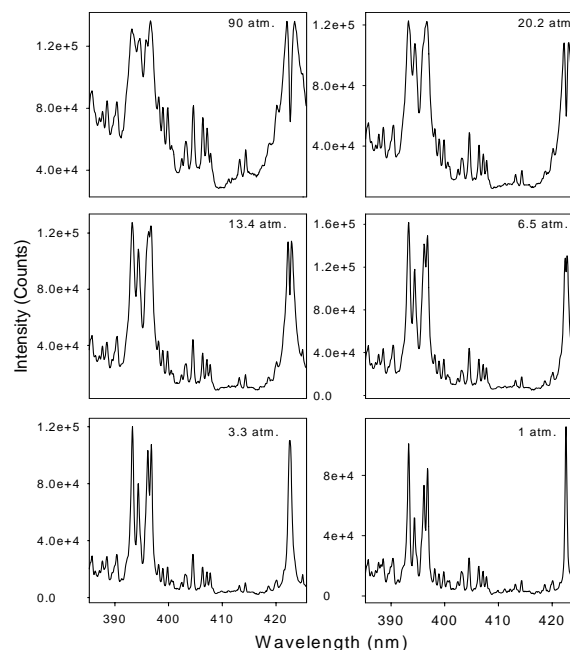


Fig. 3 LIBS spectrum of Basalt at 400 nm as a function of N₂ pressure.

Conclusions: The data presented here conclusively show the viability of using LIBS for elemental detection in an environment with pressures in the range which would be found on Venus.

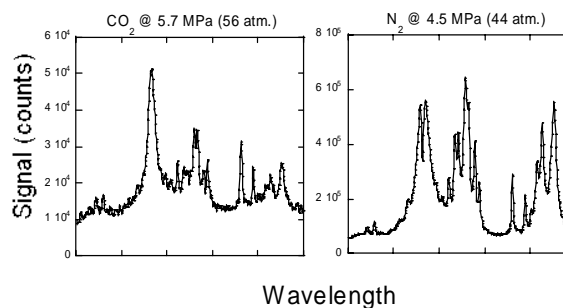


Fig. 4 Comparison of high pressure LIBS spectra in CO₂ and N₂.

References: [1] Moroz V.I. (2002) *Adv. Space Res.* 29, 215-225. [2] Iida, Y. (1989) *Appl. Spectrosc.* 43, 229-234. [3] Kuzuya M. et al. *JAAS* 7, 493-497. [4] M. Noda, Y. Deguchi, S. Iwasaki, and N. Yoshikawa, (2002) *Spectrochim. Acta*, B57, 701-709.